



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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| <b>(51) International Patent Classification <sup>6</sup>:</b><br>B05D 3/04, 3/10, D03D 3/00, 15/00,<br>B32B 9/00  | <b>A1</b> | <b>(11) International Publication Number:</b> WO 98/06508<br><b>(43) International Publication Date:</b> 19 February 1998 (19.02.98)  |
| <b>(21) International Application Number:</b> PCT/US97/13779<br><b>(22) International Filing Date:</b> 6 August 1997 (06.08.97)<br><b>(30) Priority Data:</b><br>08/693,656 9 August 1996 (09.08.96) US<br><b>(71) Applicant (for all designated States except US):</b> MTC LTD.<br>[IL/IL]; P.O. Box 4504, 91044 Jerusalem (IL).<br><b>(71) Applicant (for TJ only):</b> FRIEDMAN, Mark, M. [US/IL];<br>Alharizi 1, 43406 Raanana (IL).<br><b>(72) Inventor; and</b><br><b>(75) Inventor/Applicant (for US only):</b> TAL, Meirav [IL/IL];<br>Hagefen 51/6, 90435 Efrat (IL).<br><b>(74) Agent:</b> FRIEDMAN, Mark, M.; c/o Sheinbein, Robert, 2940<br>Birchtree Lane, Silver Spring, MD 20906 (US). |           | <b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR,<br>BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE,<br>HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS,<br>LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL,<br>PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA,<br>UG, US, UZ, VN, YU, ARIPO patent (GH, KE, LS, MW,<br>SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ,<br>MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK,<br>ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI<br>patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE,<br>SN, TD, TG).<br><br><b>Published</b><br><i>With international search report.</i> |
| <b>(54) Title:</b> METALLIZED TEXTILE<br><br><b>(57) Abstract</b><br><br>A process for activating a textile to catalyze the reduction of a metal cation, a process for metallizing the activated textile with the reduced metal, and the activated textile and metallized textile thereby produced. The textile is activated by precipitating noble metal nucleation sites on the fibers of the textile. Immersing the activated textile in a suitably prepared solution of a metal cation, and adding a reducing agent, leads to the formation of a metal plating tightly and intimately bonded to the fibers of the textile.  |           |   |

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## METALLIZED TEXTILE

### FIELD AND BACKGROUND OF THE INVENTION

5       The present invention relates to textiles and, more particularly, to a method for binding a full or partial metal plating to the fibers of a textile, and the metallized textile thereby produced.

There are a variety of applications for which a textile with a full or partial metal or metal oxide plating bonded to the fibers thereof would be  
10 useful. These include:

1.     Acaricide

Beds commonly are infested by tiny mites. These mites eat bacteria and fungi that grow on epidermal scales shed by people who sleep in the beds. Fragments of dead mites, and mite excreta, are allergens, to which  
15 asthmatics and people with dust allergens are sensitive. It has been found that some metals and metal oxides, notably Cu, CuO, Ag and Ag<sub>2</sub>O, repel mites.

The conventional method for making textiles inhospitable to mites is to treat the textiles with an organic acaricide such as benzyl benzoate.  
20 For example, Bischoff et al., in U.S. Patent No. 4,666,940, teach an acaricide that includes benzyl benzoate and a solid powder carrier whose particles are of a size suitable for ingestion by the mites. These acaricides

must be replaced every time the textile is laundered. Thus, Bischoff et al. recommend using their acaricide on textiles, such as carpets and upholstery, that are not laundered frequently. An inherently acaricidal bedsheet would keep a bed free of mites, even after multiple launderings,  
5 without the need to reapply acaricide to the bedsheet.

## 2. Bactericide and Fungicide

Some metal oxides, notably ZnO, are well known as fungicides. Before the introduction of antibiotics to medicine, silver metal sometimes was used as a bactericide and bacteriostat. Textiles with inherent  
10 bactericidal and fungicidal properties have obvious applications in settings, such as hospitals and similar institutions, where it is important to maintain aseptic conditions.

Bactericidal agents used heretofore in textiles include complexes of zirconyl acetate with inorganic peroxides (Welch et al., U.S. Patent No.  
15 4,115,422), metal cations contained in zeolite particles (Hagiwara et al., U.S. Patent No. 4,525,410), and quaternary ammonium salts (White et al., U.S. Patent No. 4,835,019; Hill et al., U.S. Patent No. 5,024,875; Zhao et al., U.S. Patent No. 5,254,134). These are not totally satisfactory, being specific to a particular textile (such as the polyamide yarn of White  
20 et al.), or being subject to eventual loss of activity by chemical decomposition, a process often hastened by laundering.

The methods known in the prior art for bonding a metal or a metal oxide to a textile generally require that the metal or its oxide be bonded indirectly to the textile. For example, the metal may be reduced to a powder and suspended in a binder. The binder-metal mixture then is  
5 applied to the textile, with the binder, and not the metal, bonding to the textile. Alternatively, the metal is reduced to a powder, an adhesive is applied to the textile, and the metal powder is spread on the adhesive. Examples of both such methods may be found in U.S. Patent No. 1,210,375, assigned to Decker. These methods are less than satisfactory  
10 for the above applications, for at least two reasons. First, the carrier or adhesive may entirely encapsulate the metal or metal oxide powder particles, inhibiting their contact with mites, fungi, and bacteria, and making the textile useless as an acaricide, fungicide, or bactericide. Second, multiple launderings tends to weaken the binder or adhesive and  
15 loosen or remove the particles.

Two notable exceptions to the general rule that metals and metal oxides have not heretofore been bonded directly to textiles are nylon  
textiles and polyester textiles, which may be plated with metals using  
standard electroless plating processes for plating plastics. The specific  
20 electroless plating methods known to the art are restricted in their applicability to only certain plastics, however. In particular, they are not suited to natural fibers, nor to most synthetic fibers.

There is thus a widely recognized need for, and it would be highly advantageous to have, a textile with a full or partial metal or metal oxide plating directly and securely bonded to the fibers thereof, for use in the applications listed above.

## 5 SUMMARY OF THE INVENTION

According to the present invention there is provided a process for activating a textile, comprising the steps of: (a) selecting the textile which includes fibers selected from the group consisting of natural fibers, synthetic cellulosic fibers, regenerated protein fibers, acrylic fibers, polyolefin fibers, polyurethane fibers, vinyl fibers, and blends thereof; (b) soaking the textile in a solution containing at least one reductant cationic species having at least two positive oxidation states, the at least one reductant cationic species being in a lower of the at least two positive oxidation states; and (c) soaking the textile in a solution containing at least one noble metal cationic species.

According to the present invention there is provided a process for metallizing a textile, comprising the steps of: (a) selecting the textile which contains fibers selected from the group consisting of natural fibers, synthetic cellulosic fibers, regenerated protein fibers, acrylic fibers, polyolefin fibers, polyurethane fibers, vinyl fibers, and blends thereof; (b) soaking the textile in a solution containing at least one reductant cationic

species having at least two positive oxidation states, the at least one cationic species being in a lower of the at least two positive oxidation states; (c) soaking the textile in a solution containing at least one noble metal cationic species, thereby producing an activated textile; and (d) 5 reducing at least one oxidant cationic species in a medium in contact with the activated textile, thereby producing a metallized textile.

According to the present invention there is provided a composition of matter comprising: (a) a textile including fibers selected from the group consisting of natural fibers, synthetic cellulosic fibers, regenerated protein 10 fibers, acrylic fibers, polyolefin fibers, polyurethane fibers, vinyl fibers, and blends thereof; and (b) a plating including materials selected from the group consisting of metals and metal oxides; the composition of matter characterized in that the plating is bonded directly to the fibers.

According to the present invention there is provided a composition 15 of matter comprising: (a) a textile including fibers selected from the group consisting of natural fibers, synthetic cellulosic fibers, regenerated protein fibers, acrylic fibers, polyolefin fibers, polyurethane fibers, vinyl fibers, and blends thereof; and (b) a plurality of nucleation sites, each of the nucleation sites including at least one noble metal; the composition of 20 matter characterized in that the nucleation sites are bonded directly to the fibers.

According to the present invention there is provided a composition of matter comprising: (a) a textile including fibers selected from the group consisting of natural fibers, synthetic cellulosic fibers, regenerated protein fibers, acrylic fibers, polyolefin fibers, polyurethane fibers, vinyl fibers, and blends thereof; and (b) a plurality of nucleation sites, each of the nucleation sites including at least one noble metal; the composition of matter characterized by catalyzing the reduction of at least one metallic cationic species to a reduced metal, thereby plating the fibers with the reduced metal.

10 In the context of the present invention the term "textile" includes fibers, whether natural (for example, cotton, silk, wool, and linen) or synthetic, yarns spun from those fibers, and woven, knit, and non-woven fabrics made of those yarns. The scope of the present invention includes all natural fibers; and all synthetic fibers used in textile applications, including but not limited to synthetic cellulosic fibers (i.e., regenerated cellulose fibers such as rayon, and cellulose derivative fibers such as acetate fibers), regenerated protein fibers, acrylic fibers, polyolefin fibers, polyurethane fibers, and vinyl fibers, but excluding nylon and polyester fibers; and blends thereof.

20 The present invention is an adaptation of technology used in the electroless plating of plastics, particularly printed circuit boards made of plastic, with metals. See, for example, Encyclopedia of Polymer Science



and Engineering (Jacqueline I. Kroschwitz, editor), Wiley and Sons, 1987, vol. IX, pp 580 - 598. As applied to textiles, this process includes two steps. The first step is the activation of the textile by precipitating catalytic noble metal nucleation sites on the textile. This is done by first  
5 soaking the textile in a solution of a low-oxidation-state reductant cation, and then soaking the textile in a solution of noble metal cations, preferably a solution of  $\text{Pd}^{++}$  cations, most preferably an acidic  $\text{PdCl}_2$  solution. The low-oxidation-state cation reduces the noble metal cations to the noble metals themselves, while being oxidized to a higher oxidation state.  
10 Preferably, the reductant cation is one that is soluble in both the initial low oxidation state and the final high oxidation state, for example  $\text{Sn}^{++}$ , which is oxidized to  $\text{Sn}^{++++}$ , or  $\text{Ti}^{+++}$ , which is oxidized to  $\text{Ti}^{++++}$ . The scope of the present invention includes this process of activation as a separate process in its own right.

15       The second step is the reduction, in close proximity to the activated textile, of a metal cation whose reduction is catalyzed by a noble metal. Examples of such cations include  $\text{Cu}^{++}$ ,  $\text{Ag}^+$ ,  $\text{Zn}^{++}$  and  $\text{Ni}^{++}$ . The reducing agents used to reduce the cations typically are molecular species, for example, formaldehyde in the case of  $\text{Cu}^{++}$ , and hydrazine hydrate in  
20 the case of  $\text{Ag}^{+++}$ . Because the reducing agents are oxidized, the metal cations are termed "oxidant cations" herein. After these oxidant cations are plated on the textile, the metal plating may be processed further, for

example, by oxidation to the oxide. This oxidation is most conveniently effected simply by exposing the metallized textile to air.

The scope of the present invention includes the metallized textiles, the oxide-plated textiles obtained by oxidizing the metallized textiles, and  
5 the intermediate activated textiles, as innovative compositions of matter in their own right. The metallized textiles and the oxide-plated textiles of the present invention are characterized in that their metal or metal oxide plating is bonded directly to the textile fibers. The plating may cover substantially all of the fiber surfaces, or may cover only part of the  
10 surfaces. Similarly, the activated textiles of the present invention are characterized in that their noble metal nucleation sites are bonded directly to the textile fibers. The activated textiles of the present invention also are characterized by their ability to catalyze the reduction of appropriate metallic cationic species, thereby plating themselves with the reduced  
15 metal.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention is of a process for binding a full or partial metallic plating to a textile, and of the metallized textiles thereby produced. Specifically, the present invention can be used to make textiles  
20 with metal and metal oxide coatings intimately and permanently bonded to the fibers of those textiles.

The principles and operation of a process for plating a textile with a metal according to the present invention may be better understood with reference to the following Examples. These Examples are illustrative, and should not be construed to restrict the scope of the present invention in any way.

#### EXAMPLE 1

A dilute acidic solution of  $\text{SnCl}_2$  was prepared by dissolving  $\text{SnCl}_2$  and concentrated  $\text{HCl}$  in water.

An dilute acidic solution of  $\text{PdCl}_2$  was prepared by dissolving  $\text{PdCl}_2$  and concentrated  $\text{HCl}$ , and water.

An 8" x 3" cotton swatch was activated as follows:

Soak in a bath of the  $\text{SnCl}_2$  solution.

Soak in a bath of the  $\text{PdCl}_2$  solution.

A dilute basic  $\text{CuSO}_4$  solution was prepared by dissolving  $\text{CuSO}_4$  and  $\text{NaOH}$  (in approximately equal weight proportions), a chelating agent, and polyethylene glycol in water.

The activated cotton swatch and formaldehyde were added to the  $\text{CuSO}_4$  solution under a pure oxygen atmosphere. After between 2 minutes and 10 minutes, the cotton swatch was removed.

The palladium deposited on the cotton swatch in the activation step catalyzed the reduction of the  $\text{Cu}^{++}$  by the formaldehyde, providing a layer of copper tightly and intimately bonded to the fibers of the cotton

swatch. The swatch, which initially was white in color, now was the color of copper metal, while retaining the flexibility and physical characteristics of the original fabric. The metallic copper color remained unchanged after several launderings.

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## EXAMPLE 2

An 8" x 3" cotton swatch was activated as in Example 1. A dilute solution of  $\text{AgNO}_3$  was prepared by dissolving  $\text{AgNO}_3$ , concentrated  $\text{NH}_4\text{OH}$ , and glacial acetic acid in water. The volume ratio of concentrated  $\text{NH}_4\text{OH}$  to glacial acetic acid was about 1.7 to 1.

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The activated cotton swatch, and dilute aqueous hydrazine hydrate, were added to the  $\text{AgNO}_3$  solution. After 10 minutes, the cotton swatch was removed.

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The palladium deposited on the cotton swatch in the activation step catalyzed the reduction of the  $\text{Ag}^+$  by the hydrazine hydrate, providing a partially oxidized layer of silver tightly and intimately bonded to the fibers of the cotton swatch. The swatch, which initially was white in color, now was dark gray. The dark gray color remained unchanged after several launderings.

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While the invention has been described with respect to a limited number of embodiments, it will be appreciated that many variations, modifications and other applications of the invention may be made.

## WHAT IS CLAIMED IS:

1. A process for activating a textile, comprising the steps of:
  - (a) selecting the textile which includes fibers selected from the group consisting of natural fibers, synthetic cellulosic fibers, regenerated protein fibers, acrylic fibers, polyolefin fibers, polyurethane fibers, vinyl fibers, and blends thereof;
  - (b) soaking the textile in a solution containing at least one reductant cationic species having at least two positive oxidation states, said at least one reductant cationic species being in a lower of said at least two positive oxidation states; and
  - (c) soaking the textile in a solution containing at least one noble metal cationic species.
2. The process of claim 1, wherein said at least one noble metal cationic species includes  $\text{Pd}^{++}$ .
3. The process of claim 1, wherein said at least one reductant cationic species is selected from the group consisting of  $\text{Sn}^{++}$  and  $\text{Ti}^{+++}$ .

4. The process of claim 3, wherein said reductant cationic species solution is aqueous.
5. The process of claim 4, wherein said reductant cationic species solution is acidic.
6. The process of claim 5, wherein said at least one reductant cationic species includes  $\text{Sn}^{++}$ .
7. The process of claim 1, wherein said noble metal solution is aqueous.
8. The process of claim 7, wherein said noble metal solution is acidic.
9. A process for metallizing a textile, comprising the steps of:
  - (a) selecting the textile which contains fibers selected from the group consisting of natural fibers, synthetic cellulosic fibers, regenerated protein fibers, acrylic fibers, polyolefin fibers, polyurethane fibers, vinyl fibers, and blends thereof;
  - (b) soaking the textile in a solution containing at least one reductant cationic species having at least two positive

- oxidation states, said at least one cationic species being in a lower of said at least two positive oxidation states;
- (c) soaking the textile in a solution containing at least one noble metal cationic species, thereby producing an activated textile; and
  - (d) reducing at least one oxidant cationic species in a medium in contact with said activated textile, thereby producing a metallized textile.

10. The process of claim 10, wherein said reduction of said at least one cationic species is effected under an oxygen atmosphere.

11. The process of claim 10, wherein said at least one noble metal cationic species includes  $\text{Pd}^{++}$ .

12. The process of claim 10, wherein said reductant cationic species is selected from the group consisting of  $\text{Sn}^{++}$  and  $\text{Ti}^{+++}$ .

13. The process of claim 12, wherein said reductant cationic species solution is aqueous, and wherein said at least one reductant cationic species is  $\text{Sn}^{++}$ .

14. The process of claim 10, wherein said noble metal solution is aqueous.

15. The process of claim 10, wherein said at least one oxidant cationic species is selected from the group consisting of  $\text{Cu}^{++}$ ,  $\text{Ag}^+$ ,  $\text{Zn}^{++}$  and  $\text{Ni}^{++}$ .

16. The process of claim 10, wherein said reducing of at least one cationic species in a medium in contact with said activated textile includes the steps of:

- (i) placing said activated textile in a solution of said at least one oxidant cationic species; and
- (ii) adding at least one reducing agent to said solution of said at least one oxidant cationic species.

17. The process of claim 16, wherein said at least one oxidant cationic species is selected from the group consisting of  $\text{Cu}^{++}$ ,  $\text{Ag}^+$ ,  $\text{Zn}^{++}$  and  $\text{Ni}^{++}$ .

18. The process of claim 17, wherein said at least one oxidant cationic species includes  $\text{Cu}^{++}$ , and wherein said at least one reducing agent includes formaldehyde.



19. The process of claim 17, wherein said at least one oxidant cationic species includes  $\text{Ag}^+$ , and wherein said at least one reducing agent includes hydrazine hydrate.

20. The process of claim 10, further comprising the step of oxidizing the metallized textile.

21. The process of claim 20, wherein said oxidizing is effected by exposing the metallized textile to air.

22. A composition of matter comprising:

- (a) a textile including fibers selected from the group consisting of natural fibers, synthetic cellulosic fibers, regenerated protein fibers, acrylic fibers, polyolefin fibers, polyurethane fibers, vinyl fibers, and blends thereof; and
- (b) a plating including materials selected from the group consisting of metals and metal oxides;

the composition of matter characterized in that said plating is bonded directly to said fibers.

23. The composition of matter of claim 22, wherein said plating materials are selected from the group consisting of Cu, Ag, Zn, Ni, CuO, Ag<sub>2</sub>O, ZnO and NiO.

24. The composition of matter of claim 22, wherein said fibers are substantially entirely covered by said plating.

25. The composition of matter of claim 22, wherein said fibers are partially covered by said plating.

26. A composition of matter comprising:

- (a) a textile including fibers selected from the group consisting of natural fibers, synthetic cellulosic fibers, regenerated protein fibers, acrylic fibers, polyolefin fibers, polyurethane fibers, vinyl fibers, and blends thereof; and
- (b) a plurality of nucleation sites, each of said nucleation sites including at least one noble metal;

the composition of matter characterized in that said nucleation sites are bonded directly to said fibers.

27. The composition of matter of claim 26, wherein said at least one noble metal includes palladium.

28. A composition of matter comprising:

- (a) a textile including fibers selected from the group consisting of natural fibers, synthetic cellulosic fibers, regenerated protein fibers, acrylic fibers, polyolefin fibers, polyurethane fibers, vinyl fibers, and blends thereof; and
- (b) a plurality of nucleation sites, each of said nucleation sites including at least one noble metal;

the composition of matter characterized by catalyzing the reduction of at least one metallic cationic species to a reduced metal, thereby plating said fibers with said reduced metal.

29. The composition of matter of claim 28, wherein said at least one noble metal includes palladium.

## INTERNATIONAL SEARCH REPORT

 International application No.  
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| <b>A. CLASSIFICATION OF SUBJECT MATTER</b><br>IPC(6) :B05D 3/04, 3/10; D03D 3/00, 15/00; B32B 9/00<br>US CL :427/304; 428/389; 442/059<br>According to International Patent Classification (IPC) or to both national classification and IPC  |   |  |
|--|---|--|
| <b>B. FIELDS SEARCHED</b><br>Minimum documentation searched (classification system followed by classification symbols)<br>U.S. : 427/304; 428/375, 379, 389, 393, 394; 442/059, 152, 153, 164, 165, 167, 170, 166; 230, 231<br>Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched<br>NONE<br>Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)<br>NONE   |   |  |
| <b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>  |   |  |
| Category*  | Citation of document, with indication, where appropriate, of the relevant passages                        | Relevant to claim No.  |
| X<br>---<br>Y  | US 4,317,856 A (HUTHWELKER et al) 02 March 1982, col. 2, lines 14-25, 34-45, 56-68; col. 3, lines 14-22.  | 1-2, 4-5, 7-9, 22-23, 25-29<br>-----<br>10-11, 14-18, 20, 21, 24                         |
| X  | US 1,210,375 A (DECKER) 26 December 1916, see entire document.  | 22-26, 28  |
| Y  | US 3,663,182 A (HAMLING) 16 May 1972, col. 1, lines 7-25, 65-70; col. 2, lines 1-43; col. 4, lines 38-45. | 1-4, 6-7, 9-17, 20-29  |
| Y  | US 4,072,784 A (CIRINO et al) 07 February 1978, col. 3, lines 50-61; Example 3.                           | 22-29  |
| <input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.   |   |  |
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| Date of the actual completion of the international search<br>03 NOVEMBER 1997  |   | Date of mailing of the international search report<br>24 NOV 1997                        |
| Name and mailing address of the ISA/US<br>Commissioner of Patents and Trademarks<br>Box PCT<br>Washington, D.C. 20231<br>Facsimile No. (703) 305-3230  |   | Authorized officer <i>Jeffrey Thomas</i><br>JILL M. GRAY<br>Telephone No. (703) 308-0651 |

# INTERNATIONAL SEARCH REPORT

International application No.  
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## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|--|-----------------------|
| Y         | US 3,860,529 A (HAMLING) 14 January 1975, col. 2, lines 4-51.                      | 22-29                 |